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# Brevet canadien / Canadian Patent

★ Le commissaire aux brevets a reçu une demande de délivrance de brevet visant une invention. Ladite requête satisfait aux exigences de la *Loi sur les brevets*. Le titre et la description de l'invention figurent dans le mémoire descriptif, dont une copie fait partie intégrante du présent document.

Le présent brevet confère à son titulaire et à ses représentants légaux, pour une période expirant vingt ans à compter de la date du dépôt de la demande au Canada, le droit, la faculté et le privilège exclusif de fabriquer, construire, exploiter et vendre à d'autres, pour qu'ils l'exploitent, l'objet de l'invention, sauf jugement en l'espèce rendu par un tribunal compétent, et sous réserve du paiement des taxes périodiques.

★ The Commissioner of Patents has received a petition for the grant of a patent for an invention. The requirements of the *Patent Act* have been complied with. The title and a description of the invention are contained in the specification, a copy of which forms an integral part of this document.

The present patent grants to its owner and to the legal representatives of its owner, for a term which expires twenty years from the filing date of the application in Canada, the exclusive right, privilege and liberty of making, constructing and using the invention and selling it to others to be used, subject to adjudication before any court of competent jurisdiction, and subject to the payment of maintenance fees.

BREVET CANADIEN

2,132,056

CANADIAN PATENT

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accordé et délivré

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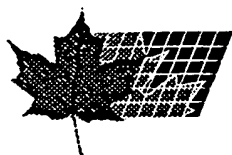
Commissaire aux brevets / Commissioner of Patents



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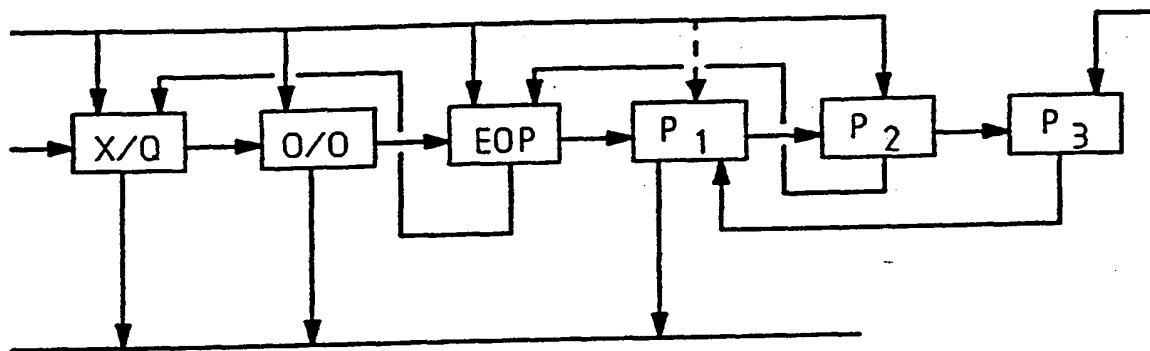
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(54) **METHODE DE BLANCHIMENT DE LA PATE**

(54) **A METHOD OF BLEACHING PULP**



(57) L'invention concerne une méthode de blanchiment de la pâte jusqu'à un degré de blanc d'au moins ISO 80 par au moins deux des agents de blanchiment suivants : oxygène, ozone, peroxyde. L'invention est caractérisée par la cuisson de la pâte, son traitement avec au moins un des agents ou processus suivants : acidification, ajout d'agents de chélation EDTA et DTPA, pour l'élimination des métaux lourds, sa délignification au cours d'un processus en deux étapes sous oxygène comprimé et son blanchiment avec au moins l'un des agents suivants : O<sub>2</sub>, O<sub>3</sub>, ClO<sub>2</sub> et H<sub>2</sub>O<sub>2</sub>.

(57) The present invention relates to a method of bleaching pulp to a brightness of at least ISO 80 by utilizing at least two of the following bleaching agents: oxygen, ozone, peroxide. The invention is characterized of cooking the pulp, treating the pulp with at least one of the following agents or manners: acidifying, EDTA and DTPA, for removing heavy metals, delignifying pulp in a pressurized, two-step oxygen stage, and bleaching the pulp with at least one of the following agents: O<sub>2</sub>, O<sub>3</sub>, ClO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>.

## A METHOD OF BLEACHING PULP

The present invention relates to a method of bleaching pulp to a brightness of at least ISO 80 by utilizing at least two of the following bleaching agents: oxygen, ozone, and hydrogen peroxide.

Efforts have been made, e.g., for environmental reasons to lessen the use of elementary chlorine in bleaching of chemical pulp. The first efforts led to use of chlorine dioxide, which as such is a better alternative than elementary chlorine in terms of environmental protection. Also marketing factors are turning the trend in the direction of total abandonment of chlorine, both elementary chlorine and compounds of chlorine. Very many customers attach great importance to the totally chlorine free (TCF) manufacture of the product they are using. Manufacture free of gaseous elementary chlorine (ECF) is regarded as the minimum requirement.

A few years ago, when ozone bleaching of medium consistency pulps had developed to a form applicable in an industrial scale (cf. FI 89516), most companies who developed processes and equipment for the pulp industry concentrated almost exclusively on ozone bleaching to develop it to a form that could be utilized in their own processes.

However, ozone has its drawbacks too. The worst of these is probably its high price, which is mainly attributable to a fairly complicated mode of manufacture. Another drawback is its high reaction activity, which means that the plants using ozone, in the same way as those using chlorine, have to be kept absolutely gas-tight. For the same reason, ozone may easily damage the cellulose itself

if the amount of dosed ozone is not exactly correct or mixing is not efficient enough.

For the above reasons, bleaching sequences have been  
5 lately supplemented with both peroxide stages and EOP  
stages, especially pressurized stages (cf. article  
"Medium consistency pulp washer generates superior  
washing efficiency", TAPPI Journal, June 1990;  
PCT/FI92/00198, published as WO93/00470, January 7, 1993;  
10 EU patent 557,112, published August 25, 1993;  
PCT/FI93/00222, published as WO94/20673, September 15,  
1994). However, it becomes apparent from the above  
publications that the role of ozone is still of great  
significance in bleaching sequences.

15 The present invention strives for paying attention to  
both environmental values, which are turning the trend  
away from chlorine chemicals, and economic points of  
view, which are to at least some extent opposed to use of  
ozone. The method of the present invention enables  
20 bleaching of pulp up to a brightness of 83 to 85 ISO or  
even to a higher brightness, with no need to use either  
chlorine or ozone. If, however, a still higher  
brightness is desired, one peroxide stage of the sequence  
according to the invention is replaceable by an ozone  
25 stage. In this way, a brightness of ISO 90 is readily  
achievable. Correspondingly, it is also possible to use  
much less chlorine dioxide than before for the production  
of fully bleached pulp.

The characteristic features of the method of the  
30 invention are best seen from the accompanying claims.

The method of the invention is described in more detail  
in the following, by way of example, with reference to  
the enclosed drawings in which

- Fig. 1 shows a preferred embodiment of the bleaching sequence according to the invention;  
Fig. 2 is a graphic illustration of a significant benefit gained by the invention; and  
5 Fig. 3 shows a preferred subprocess of the bleaching sequence in accordance with the invention.

10 The bleaching sequence X/Q-O/O-EOP-P<sub>1</sub>-P<sub>2</sub>-P<sub>3</sub> of the embodiment shown in Fig. 1 is started with a previously known Q stage, the purpose of which is to remove heavy metals from the cellulose pulp by chelating (e.g., EDTA, DTPA or equivalent compounds) or acidifying in order to prevent them from impeding the peroxide stages (P<sub>n</sub>) which follow. In this stage, it is also possible to treat the pulp with  
15 enzymes (denoted with X), which expose the lignin considering later delignification stages. The oxygen stage O/O, which comes next, is actually formed of two or more pressurized oxygen delignification stages or steps with no wash therebetween, as described in greater detail in  
20 connection with Fig. 2. The third stage, EOP (alkalic bleaching extraction), which is separated from the O/O stage with wash, is disclosed, e.g., in article "Medium consistency pulp washer generates superior washing efficiency", TAPPI Journal, June 1990. The peroxide stages  
25 (P<sub>n</sub>) which come next in the sequence and which are preferably pressurized but may also be atmospheric, are correspondingly disclosed, e.g., in PCT/FI92/00198 published January 7, 1993. The use of a pressurized reactor is advantageous especially when gaseous chemicals, such as  
30 oxygen, are used or when gaseous chemical is generated in the reactor, as happens when hydrogen peroxide splits into water and active oxygen.

35 Fig. 1, on the other hand, illustrates an advantageous arrangement for circulating wash liquid in the bleaching sequence. In other words, washing after the last bleach-

ing stage,  $P_3$  in this case, is effected with white water. The filtrate thereby resulted is conveyed over the preceding bleaching stage  $P_2$  to serve as the wash liquid of the washer in stage  $P_1$ . The washer of stage  $P_2$  is supplied  
5 with fresh water of about  $75^\circ\text{C}$  to serve as the wash liquid therein. The filtrate from stage  $P_2$ , or at least a portion thereof, is conveyed to the washing stage after EOP to serve as a wash liquid therein. The filtrate received therefrom is taken to the washing stage follow-  
10 ing the metal removal Q. The circulation of the filtrate from the washing in stage  $P_2$  especially results in that the peroxide which has come from the stage  $P_2$  and entered the filtrate ends up in the oxygen stage and intensifies its delignification reaction. If we go further in the  
15 process, it is possible that the peroxide-containing filtrate from a washer of some other bleaching stage, e.g.,  $P_1$  or  $P_3$ , is taken to the washing stage of brown-stock. Thus, peroxide is taken also via this route to the delignification stages.

20

The reason for connecting two oxygen stages in sequence, as in Fig. 1, is shown in Fig. 2. The vertical axis indicates the kappa number and the horizontal axis the time used for the process. Graph a) shows a conventional  
25 advance of a bleaching process. In other words, as soon as the chemicals have been mixed with the pulp, the kappa number of the pulp declines sharply. Later it becomes steady to such an extent that an extension of time does not bring an essential change to the reaction result.  
30 Naturally, there are various reasons for that. Firstly, consumption of the chemical slows down the declining of the kappa number. Secondly, more and more reaction products are formed in the suspension nearest to the fibers all the time, whereby the unreacted chemical still present  
35 in the suspension does not easily access the fibers. Thirdly, the amount of lignin present in the fibers

decreases, whereby its detachment from the fibers in proportion takes place more slowly. And fourthly, because pulp always contains some amount of gas, the gas which is contained by the pulp after mixer and being in the form of micro bubbles tends to accumulate by nature and produce bigger bubbles, which impede mass transport in the pulp suspension. Bubbles are also generated as product of bleaching reactions. Such reactions may be, for example, the splitting of hydrogen peroxide into water and active oxygen. A new mixing stage breaks big bubbles into micro bubbles. Thus, it may be estimated that mixing alone somewhat improves the treatment result. Graph b) indicates what happens if the first reaction is in a way interrupted at point  $t_1$ , a new portion of chemical is dosed to the suspension, and is mixed therewith evenly and efficiently. It can be seen that the shape of graph b) is equal to the shape of graph a) after the chemical addition. A comparison between the kappa numbers indicated by graphs a) and b) when time  $t_2$  has passed reveals that the procedure in accordance with graph b) brings a considerably lower kappa number than the procedure illustrated by graph a). It is naturally conceivable that chemical could be added once more to the suspension, and obtain a still lower kappa number in the same time and practically with the same amount of chemicals.

Fig. 3 illustrates slightly more in detail an implementation of the O/O stage in a sequence of a preferred embodiment of the invention. Outermost in the left is shown a washer, denoted with reference numeral 10, which effects removal of heavy metals from the pulp. The washer may be, e.g., A. AHLSTROM CORPORATION's DD-washer or Kamyr Inc.'s pressure diffuser. After washer 10, the pulp is conveyed to a steam mixer 12 for raising its temperature, and further via an intermediate tank 14 by pump 16 into a mixer 18, where pulp is mixed with at least oxygen as a

bleaching chemical and sodium hydroxide for pH regulation. If it is desirable to add a little peroxide to this oxygen stage, it can be mixed with the same mixer 18. Steam and/or magnesium, preferably magnesium sulphate, may also be mixed by mixer 18. Mixer 18 is replaceable with an MC pump provided with at least one chemical feed conduit, in which case the pump 16 posterior to the steam mixer 12 could substitute for mixer 18. A precept for mixing chemicals, especially oxygen, is a division ratio 60/40. In other words, the first stage is supplied with 60% of the total amount of oxygen and the second with 40%. In general, the chemical dosage for the first oxygen step is 5 to 20 kgO<sub>2</sub>/admt and, if peroxide is fed to the first stage, the dosage is relatively small, only about 1 to 10 kg/admt. From the mixer 18, pulp is discharged and fed to a reaction tower 20, where the pH value is kept within the range of 9 to 13, preferably 10 to 11.5, the temperature within the range of 75 to 110°C, preferably 85 to 95°C, and the pressure within 2 to 15 bar, preferably 3 to 10 bar. The retention time in the first reaction tower 20 is about 10 to 60 minutes, preferably 25 to 50 minutes.

From the tower 20, pulp is discharged with a discharge means 22 via a second mixer 24 to a second reaction tower 28. The discharge means may be means which is capable of gas separation, thereby eliminating the above described gas problem (e.g., means disclosed in WO patent applications PCT/FI90/00085 published as WO93/01875 February 4, 1993 and PCT/FI92/00216 published as WO90/13344 November 15, 1990). Preferably pulp is fed to the reaction tower 28 with a distributing means 26, which ensures that the pulp column grows evenly in the tower 28 and that no channelling takes place. Said distributing means is described, e.g., in U.S. patent 4,964,950 published October 23, 1990, and its use for the above described purpose is dealt with in FI patent application 924805 published April 24, 1994. The chemical dosages in mixer 24 are as follows: 5 to 20 kgO<sub>2</sub>/admt and



about 5 to 40 kg/admt peroxide; the whole peroxide dosage preferably added to this second step. The pH value is kept, by feeding sodium hydroxide, in this second oxygen step within the range of 9 to 13, preferably 10 to 11.5, the temperature within 75 to 110°C, preferably 85 to 95°C, and the pressure within 2 to 10 bar, preferably 3 to 5 bar. The retention time in the second reaction tower 28 is about 30 to 100 minutes, preferably 45 to 90 minutes. From the tower 28, the pulp is discharged via discharge means 30, which separates gas if necessary, to a blow tank 32, wherefrom it is conveyed by a pump 34 to a washer 36. If gas is separated by discharge means, it is advantageous to lead the gas into the blow tank 32.

A second embodiment of the bleaching method according to the invention is a bleaching sequence, by which a pulp brightness of ISO 90 is obtained. In this sequence, the first peroxide stage of the sequence shown in Fig. 1 is replaced with an ozone stage. In other words, the sequence will be

X/Q-O/O-EOP-Z-P-P.

An alternative sequence is naturally  
Q-O/O-EOP-Z-P-P,  
from which the enzyme treatment has been left out.

To the above sequence may also be applied a combination of medium consistency ozone bleaching and pressurized peroxide stage, which is described, for example, in WO patent application PCT/FI92/00198 published January 7, 1993. In that case, the sequence will be

X/Q-O/O-EOP-ZP-P-P.

When the enzyme treatment is omitted, the sequence will be

Q-O/O-EOP-ZP-P-P.

Other applicable sequences, characteristic of the method of the invention. are, for example, the following:

O-Q-O/O-P<sub>n</sub>,

which is started with oxygen delignification and continued with the sequence described above. For example, in this sequence a great benefit is gained if one of the filtrates of peroxide stages P<sub>n</sub> is introduced into a washing stage preceding the oxygen delignification O. It is also possible to add some peroxide to said oxygen delignification stage for making this more efficient. With this sequence, a brightness of up to ISO 85 is obtained. If the brightness of ISO 90 is desired, an ozone stage may be added before the peroxide stage as follows:

O-Q-O/O-Z-P<sub>n</sub>, or

O-Q-O/O-Z/Z-P<sub>n</sub>,

where Z/Z means more than one ozone bleaching step as described, e.g., in FI publication 89516. In practice, this is effected so that ozone is mixed with pulp by and from a plurality of mixers sequentially, without any pulp washing therebetween. Gas may be discharged from these ozone steps, as disclosed in WO patent application PCT/FI92/00276 published April 29, 1993, so that a new addition of ozone would bring in proportion a bigger dosage of ozone into the pulp. Naturally, also the following sequences are applicable:

O-Q-O/O-ZP-P<sub>n</sub>,

O-Q-O/O-ZP,

O-Q-O/O-Z/ZP, and

O-Q-O/O-Z/ZP-P<sub>n</sub>

#### Example 1

A pulp mill had the sequence

D<sub>0</sub>-O-EOP-D<sub>1</sub>-E-D<sub>2</sub>

in use, where D denotes a chlorine dioxide stage in general. A normal dosage in this case is about 40 kg active

chlorine/admt, i.e., about 15 kg ClO<sub>2</sub>/admt. When the oxygen stage O was replaced with a two-step oxygen stage O/O, in other words

D<sub>0</sub>-O/O-EOP-D<sub>1</sub>-E-D<sub>2</sub>

5 the chlorine dosage to the stage D<sub>0</sub> could be reduced to a value 15 kg active chlorine/admt, i.e., to 5.7 kg ClO<sub>2</sub>/admt, in other words over 60%. Regarding the whole sequence, the change in the consumption of active chlorine was about 70 -> 45 kg Cl/admt, i.e., of the order of  
10 35%. The AOX reduction which is often used as a measure of environmental loading, is over 50%, i.e., < 1.0 kg/admt. The O/O stage may also be safely supplied with peroxide because the D<sub>0</sub> stage is as such a highly efficient remover of heavy metals.

15

Tests performed have given the following kappa numbers and brightness values in various stages.

		D <sub>0</sub>	O/O <sub>p</sub>	EOP	D <sub>2</sub>
20	Kappa	16	3	3	<0.1
	Brightness		50	83	90

The above results indicate that the D<sub>0</sub> stage may be modified so that it only removes heavy metals and activates  
25 lignin, whereafter the O/O stage in accordance with a preferred embodiment of the invention, intensified with peroxide, is very efficient.

#### Example 2

30

A pulp mill used the bleaching sequence

D<sub>1</sub>/O-O/O-E<sub>op</sub>-D<sub>2</sub>-E,

35 by which a brightness of ISO 90 was achieved. However, since the sequence further had two chlorine dioxide

10

stages, the mill wanted to substitute some other chemical for chlorine. They ended up to replace the second chlorine-using stage, D<sub>2</sub>, with one or more peroxide stages and the first chlorine-using stage D<sub>1</sub> with a stage X/Q, which  
 5 activates lignin and removes heavy metals, and in which, for example, EDTA, DTPA or equivalent and enzymes (X stage) are used. Thus, the resulting bleaching sequence was

X/Q-O/O-EOP-P<sub>1</sub>-P<sub>2</sub>-P<sub>3</sub>.

10

The dosages (kg/admt) in the test performed were in accordance with Table 1 below. Table 2 shows the corresponding process parameters. The production rate in the test was 500 admt/d. NaOH is not always added to the P stage  
 15 (P<sub>2</sub> in Table 1) preceding the last P stage. When the pH is remains lower, pulp is activated and delignified prior to the last P stage. An appropriate pH in such a stage may be 3-7, most preferably approximately 5.

20 Table 1

	X/Q	O/O	EOP	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
25	NaOH	25	5	11		7
	O <sub>2</sub>	20	6			
30	H <sub>2</sub> O <sub>2</sub>	5	7	40	5	21
	H <sub>2</sub> SO <sub>4</sub> 5					
	EDTA 3					
35	DTPA	2	2			
	MgSO <sub>4</sub>	3	2			
	Enzyme 5 - 10					
40	SO <sub>2</sub>					3

Table 2

	X/Q	O/O	EOP	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	
5	Temperature	40	95	80	85	70	85
10	Retention	50	150	25+100	180	60	180
	Kappa	15.2	<8	<5	<3		<2
	Brightness	34	45	65	75	77	>83
15	pH	5.5	11	11			

20 In the best succeeded trial, even > 85 ISO brightness was achieved, which was much better than expected. The addition of peroxide to<sup>s</sup> the oxygen stage O/O raised the brightness values considerably, i.e., from 45 to 55 ISO. The kappa number again declined from 15 to 5 without an addition of peroxide, but when peroxide was added, from 25 15 to 4.

Generally speaking, a bleaching sequence Q-O/O-EOP-P<sub>1</sub>-P<sub>2</sub>-P<sub>3</sub> with dosages (kg/admt) shown in Table 3 below, results in pulp the quality of which is good and the manufacturing costs of which are not high. Below each range is shown a dosage which has proven especially advantageous in our tests, but such values have to be considered approximate.

### 35 Example 3

In tests with pressurized peroxide bleaching, it was found, among other things, that the same bleaching result, with regard to both brightness and kappa number, 40 as was earlier received unpressurized with three hours' treatment was now received in one hour when the pressure was about 5 bar. Further, the tests revealed that pres-

surized treatment also considerably improved the effect of chelating agents, such as EDTA and DTPA. The improvement even seems to make it possible to totally give up a separate discharge stage of heavy metals and to effect chelating of heavy metals in connection with each peroxide-using delignification/bleaching stage. Thus, the nowadays very popular unpressurized sequence

Q-P-Z-P

could be replaced with a sequence

10 P-Z-P,

in which the P stages are pressurized and they, or at least the first of them, could be supplied with chelating agents for binding heavy metals.

15 Pressurized peroxide stages also facilitate replacement of the above described sequence Q-O/O-EOP-P<sub>n</sub> by a sequence

Q-O/O-P<sub>n</sub>,

by which a brightness as high as ISO 85 is achieved. When a brightness of ISO 90 is desired, the peroxide stage may be replaced with a combined ozone and peroxide stage

20 Q-O/O-ZP.

As can be seen from the above description, a novel environmentally friendly bleaching method has been developed, which facilitates removal of the earlier used bleaching stages, which employ both elementary chlorine and compounds of chlorine, and lessens the use of expensive ozone. However, it is to be noted that the above description handles only a few exemplary embodiments of the bleaching method of our invention, and it is by no means intended to limit the invention from what is disclosed in the accompanying claims. Thus, it is for example self-evident that also in those sequences where the feed of enzymes to the metal removal stage has not been separately disclosed, such feed is possible.

Table 3

	Q	O <sub>1</sub>	O <sub>2</sub>	EOP	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>
EDTA	0-5 3						
DTPM	0-5 3						
Enzyme	0.5-1.0 0.5						
H <sub>2</sub> SO <sub>4</sub>	2-10 3						
O <sub>2</sub>	5-20 15	5-20 10	2-8 4				
H <sub>2</sub> O <sub>2</sub>		1-10 5	5-40 15	1-10 5	10-40 30	5-30 10	0-40 20
NaOH		10-30 20	2- 10 4	5-10 5	5-20 10	2-10 5	5-20 10
MgSO <sub>4</sub>		0-8 3		1-5 2			1-3 2

**CLAIMS**

1           1.       A method of bleaching pulp by elemental chlorine-free process to  
2   a brightness of at least ISO 80 by utilizing at least two of the following  
3   bleaching agents: oxygen, ozone, peroxide,  
4   wherein the following stages are performed:  
5   a)     cooking of the pulp,  
6   b)     treating of the pulp with at least one of the following agents or manners,  
7   for removing heavy metals:  
8   acidifying, chelation,  
9   c)     delignification of the pulp in an oxygen stage (O/O), which has two or  
10  more steps, with no wash therebetween, and  
11  d)     bleaching of the pulp with at least one of the following: O<sub>2</sub>, O<sub>3</sub>, ClO<sub>2</sub>,  
12  H<sub>2</sub>O<sub>2</sub>.

1           2.       A method as recited in claim 1, wherein in stage d) the pulp is  
2   first bleached in the alkaline stage using oxygen and peroxide (EOP) and  
3   thereafter in at least one peroxide stage.

1           3.       A method as recited in claim 1, wherein the oxygen stage in c) is  
2   pressurized.

1           4.       A method as recited in claim 1, wherein the oxygen stage O/O  
2   uses peroxide to intensify the delignification reaction.

1           5.       A method as recited in claim 1, wherein the pulp is cooked to  
2   kappa number 25, in stage a).

1           6.       A method as recited in claim 1, wherein the oxygen dosage to the  
2   first step is 5 to 20 kg/admt.

1           7.       A method as recited in claim 4, wherein the first step is supplied  
2   with 0 to 10 kg/admt of peroxide.



1           8.     A method as recited in claim 3, wherein in the first step, the  
2     temperature is 75 to 110°C, the pressure is 2 to 15 bar, and the pH is 9 to  
3     13.

1           9.     A method as recited in claim 3, wherein the second step is  
2     supplied with 5 to 20 kg/admt of oxygen.

1           10.    A method as recited in claim 4, wherein the second step is  
2     supplied with 5 to 40 kg/admt of peroxide.

1           11.    A method as recited in claim 3, wherein in the second step the  
2     temperature is 75 to 110°C, the pressure is 2 to 10 bar, and the pH is 9 to  
3     13.

1           12.    A method as recited in claims 2 and 3, wherein the bleaching  
2     sequence is Q-O/O-EOP-P<sub>n</sub>, where Q denotes metal removal, O oxygen stage,  
3     EOP bleaching alkalic extraction stage and P<sub>n</sub> generally one or more peroxide  
4     stages, and marking "-" denotes washing between the various stages.

1           13.    A method as recited in claim 2, wherein at least one of the  
2     peroxide stages is replaced with an ozone stage for reaching a higher final  
3     brightness, whereby the sequence is either Q-O/O-EOP-Z-P or Q-O/O-EOP-ZP-  
4     P, where Z denotes ozone bleaching.

1           14.    A method as recited in claim 3, wherein one of the following  
2     bleaching sequences is used:  
3                Q-O/O-P<sub>n</sub>,  
4                Q-O/O-ZP,  
5                O-Q-O/O-P<sub>n</sub>,  
6                O-Q-O/O-Z-P<sub>n</sub>,  
7                O-Q-O/O-Z/Z-P<sub>n</sub>,  
8                O-Q-O/O-ZP-P<sub>n</sub>,  
9                O-Q-O/O-ZP,  
10              O-Q-O/O-Z/ZP,  
11              O-Q-O/O-Z/ZP-P<sub>n</sub>, where

- 12 O denotes a one-step oxygen delignification stage,
- 13 Q denotes a metal removal stage using chelating agents or acidation,
- 14 O/O denotes a two-step oxygen delignification stage,
- 15 Z/Z denotes an ozone bleaching stage with two or more steps, and
- 16 P<sub>n</sub> denotes one or more successive peroxide stages.

1           15. A method as recited in claim 3, wherein one of the following  
2 bleaching sequences is used:

3           D<sub>0</sub>-O/O-EOP-D-E-D,

4           D<sub>0</sub>-O/O-EOP-DE, in which

5 D<sub>0</sub> denotes an activating and metals removing chlorine dioxide stage, and

6 D denotes a conventional bleaching chlorine dioxide stage.

1           16. A method as recited in claim 12, 13 or 14, wherein at least a  
2 portion of the filtrate received from the washing stage posterior to a peroxide  
3 stage is conveyed to a washing stage preceding the oxygen stage in order to  
4 conduct the residual peroxide to the oxygen stage for intensifying thereof.

1           17. A method as recited in claim 2, wherein 2 to 8 kg/admt of oxygen  
2 and 0 to 10 kg/admt of peroxide are added to the EOP stage.

1           18. A method as recited in claim 17, wherein magnesium is added to  
2 the EOP stage.

1           19. A method as recited in claim 1, wherein magnesium is added to  
2 the oxygen stage c).

1           20. A method as recited in claims 6 and 9, wherein the bleaching  
2 sequence is Q-O/O-EOP-P<sub>1</sub>-P<sub>2</sub>-P<sub>3</sub>, whereafter the kappa number of pulp is <  
3 2.0 and brightness > 83.

1           21. A method as recited in claims 7 and 10, wherein the bleaching  
2 sequence is Q-O/O-EOP-P<sub>1</sub>-P<sub>2</sub>-P<sub>3</sub>, whereafter the pulp kappa number is < 2 and  
3 the brightness > 85.

1 22. A method as recited in claim 20 or claim 21, wherein peroxide is  
2 added to the P stages, 25 to 110 kg/admt in total.

1 23. A method as recited in claim 20 or claim 21, wherein 10 to 40  
2 kg/admt of peroxide is added to the P<sub>1</sub> stage.

1 24. A method as recited in claim 20 or claim 21, wherein 5 to 30  
2 kg/admt of peroxide is added to the P<sub>2</sub> stage.

1 25. A method as recited in claim 20 or claim 21, wherein 10 to 40  
2 kg/admt of peroxide is added to the P<sub>3</sub> stage.

1 26. A method as recited in one of claims 12, 13, 14, 20 or 21,  
2 wherein the Q stage is combined with a lignin activating treatment with  
3 enzyme (X).

1 27. A method as recited in one of claims 12, 13, 14, 20, or 21,  
2 wherein at least one of said P stages is pressurized.

1 28. A method as recited in one of claims 2, 4, or 27, wherein at least  
2 one of said pressurized stages using peroxide is supplied with chelating agents.

1 29. A method as recited in claim 1, wherein pulp is bleached in at  
2 least one of the stages c) and d) in at least one stage utilizing peroxide without  
3 the addition of NaOH.

1 30. A method as recited in claim 14, wherein in a sequence utilizing  
2 several peroxide stage the pH of the last but one stage is lower.

1 31. A method as recited in claim 1, 29 or 30, wherein peroxide is  
2 added to the O/O stage.

1 32. A method as recited in 31, wherein the bleaching sequence is O-  
2 Q-O/Op-Pa-P, in which O/Op denotes an O/O stage, to which peroxide is

3 add d, and Pa and P denote stages without alkali addition, wher by the pH  
4 thereof is lower.

1 33. A method as recited in one of claims 1, 29, 30, 31 or 32, wherein  
2 all stages are pressurized.

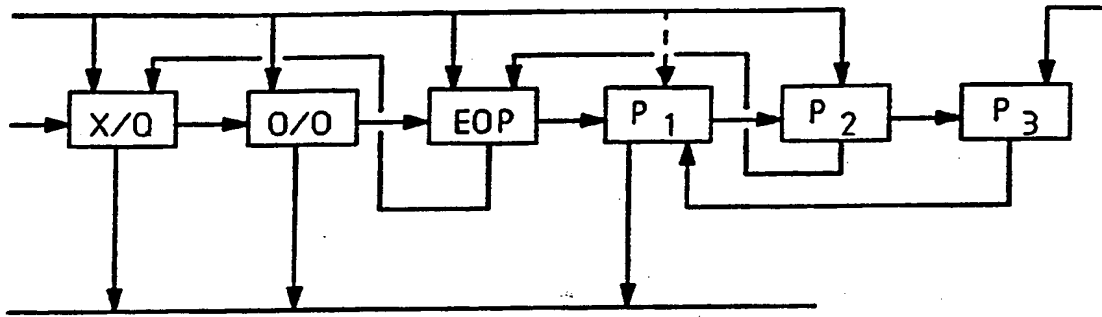


FIG. 1

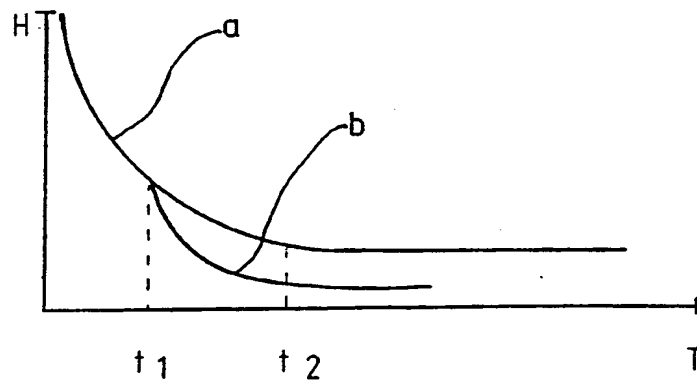


FIG. 2

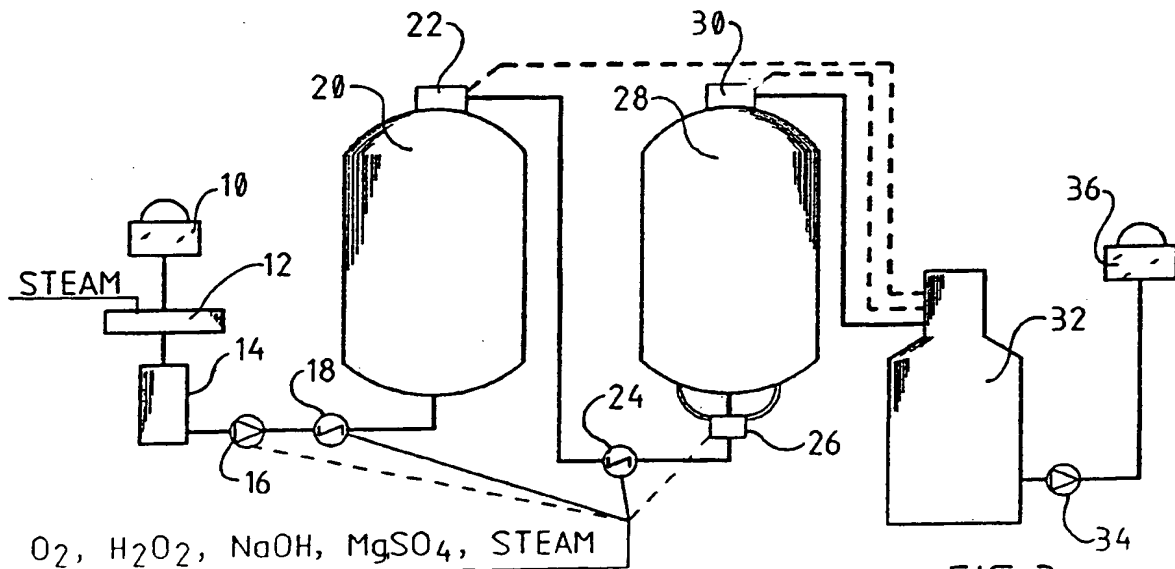


FIG. 3

